

PATENT SPECIFICATION

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(54) PRODUCTION OF PHTHALIDE CARBOXYLIC ACID-(5)

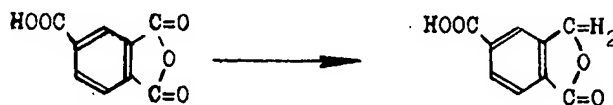
(71) We, BASF AKTIENGESellschaft, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

This invention relates to a process for the production of phthalide carboxylic acid-(5). Phthalide carboxylic acid-(5) is an interesting intermediate for example for the active ingredient and dye fields and for condensation products, particularly for resins for surface coatings.

Prior art methods of producing phthalide carboxylic acid-(5) are troublesome and comprise several steps. Thus for example phthalide carboxylic acid may be obtained by condensing the dimethyl ester of Δ-1,4-dihydroterephthalic acid and an oxalic ester to form an ester of phthalide dicarboxylic acid-(3,5) and subjecting this condensation product to a thermal treatment at 240°C (see Berichte der Deutschen Chemische Gesellschaft, 36, 843).

According to the present invention there is provided a process for the production of phthalide carboxylic acid-(5) which comprises subjecting trimellitic anhydride to electrochemical hydrogenation in aqueous solution at a temperature below 100°C.

According to the process of the invention trimellitic anhydride can be converted in a single step and in a good yield with high selectivity into phthalide carboxylic acid-(5):—



The aqueous solution of trimellitic anhydride to be used according to the invention generally has a trimellitic anhydride content of from 1 to 30%, preferably 5 to 15%, by weight. The aqueous solution preferably also contains ammonia, with an ammonia content generally of up to 20%, and preferably from 5 to 15%, by weight. The aqueous solution may also contain for example up to 50% by weight of an organic solvent which is miscible with water. Examples of such solvents are alcohols such as methanol or ethanol; ethers such as tetrahydrofuran and dioxane; amides such as dimethylformamide; and nitriles such as acetonitrile. The aqueous solution may also contain for example up to 20% by weight of an ammonium salt such as ammonium carbonate; its pH should advantageously be more than 7.

In the electrochemical hydrogenation the above aqueous solution forms the catholyte and it is convenient to use an aqueous mineral acid, preferably aqueous sulfuric acid, as the anolyte.

The process according to the invention may be carried out in a conventional electrolytic cell. It is preferred to use a cell in which the anode compartment and the cathode compartment are separated by a diaphragm, for example a porous clay diaphragm or a commercial ion exchange membrane, as in a cell of the filter press type having bipolar electrodes in plate form. Cation exchanger membranes and particularly those of the type containing fluorine are especially suitable as diaphragms.

The electrochemical hydrogenation may be carried out for example at temperatures of from 10° to 95°C and preferably at from 20° to 50°C.

5 The cathode(s) conveniently consist of a metal having adequately high hydrogen overvoltage (more negative than -0.5 volt) such as mercury, lead, cadmium or antimony. Lead has proved to be particularly suitable. The surface of the cathode may be structured to increase the active surface area. 5

The anodes used may be made of the anode materials disclosed in the literature, such as graphite, manganese dioxide, precious metals, titanium doped with a precious metal oxide or, preferably, lead dioxide.

10 The current density in the electrolysis may be for example from 1 to 30 A/dm² and particularly from 3 to 15 A/dm². 10

To achieve a high cathode activity with a high current efficiency and a high conversion in continuous sustained operation, it may be advantageous to switch off the direct current after a certain period of electrolysis, for example after from half an hour to ten hours, for example for a period of from half a minute to three minutes, the electrodes thus being short-circuited during these periods. 15

After the electrolysis, working up may be carried out by evaporating the electrolysis product to dryness, taking up the residue in water and acidifying with mineral acid to isolate the phthalide carboxylic acid. The precipitated product can then be filtered off, washed with water and dried. 20

The following Example illustrates the invention.

EXAMPLE

25 250 g of trimellitic anhydride is added, while stirring, to a solution of 36 g of ammonium carbonate in 400 g of 25% aqueous ammonia solution. Another 1500 g of water is then added to complete the dissolution of the suspension. The solution is pumped continuously, via a reservoir, through an electrolytic cell of the filter press type. The anode and cathode compartments are separated by a cation exchanger membrane containing fluorine. The cathode consists of lead and has a surface area of 2.3 dm². The anode consists of lead oxide on lead. The anolyte consists of 5% 30 sulfuric acid. The current density is 5 A/dm²; the reaction temperature is 24°C. After a period of electrolysis of twenty hours (the direct current being switched off every hour and the cell short-circuited for one minute) the reaction is over. The electrolysis product is worked up by evaporating it to dryness in a circulation evaporator in vacuo at 80°C. The residue is dissolved in a small amount of water and 50% sulfuric acid is added at 80°C. The whole is stirred for one hour at this 35 temperature and then cooled to 5°C. The precipitate is filtered off and washed with ice water. 225 g of pure phthalide carboxylic acid-(5) having a melting point of 227° to 228°C is obtained. Conversion is 100% and selectivity is 89.5%. 35

WHAT WE CLAIM IS:—

40 1. A process for the production of phthalide carboxylic acid-(5) wherein trimellitic anhydride is electrochemically hydrogenated in aqueous solution at a temperature below 100°C. 40

2. A process as claimed in claim 1 wherein the trimellitic anhydride is treated in an aqueous ammoniacal solution.

45 3. A process as claimed in claim 1 or 2 wherein the aqueous solution contains from 1 to 30% by weight of trimellitic anhydride. 45

4. A process as claimed in claim 2 or 3 wherein the aqueous solution contains up to 20% by weight of ammonia.

50 5. A process as claimed in any of claims 1 to 4 wherein the electrochemical hydrogenation is carried out at a temperature of from 10° to 95°C. 50

6. A process as claimed in any of claims 3 to 5 wherein the aqueous solution contains from 5 to 15% by weight of trimellitic anhydride.

7. A process as claimed in any of claims 4 to 6 wherein the aqueous solution contains from 5 to 15% by weight of ammonia.

55 8. A process as claimed in any of claims 1 to 7 wherein the aqueous solution contains up to 50% by weight of a solvent which is miscible with water. 55

9. A process as claimed in any of claims 1 to 8 wherein the aqueous solution contains up to 20% by weight of an ammonium salt.

60 10. A process as claimed in any of claims 5 to 9 wherein the electrochemical hydrogenation is carried out at a temperature of from 20° to 50°C. 60

11. A process as claimed in any of claims 1 to 10 wherein the aqueous solution has a pH of more than 7.

12. A process as claimed in any of claims 1 to 11 carried out in a cell having anode and cathode compartments separated by a diaphragm formed by a cation exchanger membrane, the aqueous solution of trimellitic anhydride forming the catholyte.

5 13. A process as claimed in claim 12 wherein the anolyte is an aqueous mineral acid. 5

14. A process as claimed in any of claims 1 to 13 wherein the electrochemical hydrogenation is carried out at a current density of from 1 to 30 A/dm².

10 15. A process as claimed in claim 14 wherein the current density is from 3 to 15 A/dm². 10

16. A process as claimed in any of claims 1 to 15 wherein the direct current is switched off for at least one period during the electrochemical treatment, during which period the electrodes are short-circuited.

15 17. A process for the production of phthalide carboxylic acid-(5) carried out substantially as described in the foregoing Example. 15

18. Phthalide carboxylic acid-(5) when obtained by the process claimed in any of claims 1 to 17.

19. Dyes and surface coating resins when obtained from phthalide carboxylic acid-(5) claimed in claim 18.

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